

# REAL-TIME OPTICAL MONITORING AND SIMULATIONS OF GAS PHASE KINETICS IN InN VAPOR PHASE EPITAXY AT HIGH PRESSURE

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## Abstract

Understanding the kinetics of nucleation and coalescence of heteroepitaxial thin films is a crucial step in controlling a chemical vapor deposition process, since it defines the perfection of the heteroepitaxial film both in terms of extended defect formation and chemical integrity of the interface. The initial nucleation process also defines the film quality during the later stages of film growth. The growth of emerging new materials heterostructures such as InN or In-rich  $\text{Ga}_x\text{In}_{1-x}\text{N}$  require deposition methods operating at higher vapor densities due to the high thermal decomposition pressure in these materials. High nitrogen pressure has been demonstrated to suppress thermal decomposition of InN, but has not been applied yet in chemical vapor deposition or etching experiments. Because of the difficulty with maintaining stoichiometry at elevated temperature, current knowledge regarding thermodynamic data for InN, e.g., its melting point, temperature-dependent heat capacity, heat and entropy of formation are known with far less accuracy than for InP, InAs and InSb. Also, no information exists regarding the partial pressures of nitrogen and phosphorus along the liquidus surfaces of mixed-anion alloys of InN, of which the  $\text{InN}_x\text{P}_{1-x}$  system is the most interesting option. A miscibility gap is expected for  $\text{InN}_x\text{P}_{1-x}$  pseudobinary solidus compositions, but its extent is not established at this point by experimental studies under near equilibrium conditions. The extension of chemical vapor deposition to elevated pressure is also necessary for retaining stoichiometric single phase surface composition for materials that are characterized by large thermal decomposition pressures at optimum processing temperatures.

## Introduction

In this paper we describe our progress in establishing a high-pressure chemical vapor deposition (HPCVD) system with integrated real-time optical monitoring capabilities[1-3]. The objective of this work is the real-time evaluation of the growth kinetics of nucleation and coalescence of heteroepitaxial thin films, which is an important step of chemical vapor deposition since it defines the perfection of the heteroepitaxial film both in terms of extended defect formation and chemical integrity of the interface. Presently, most growth efforts focus on low pressure processing to minimize the influence of flow dynamics on process uniformity and favors for III-V compounds organometallic chemical vapor deposition (OMCVD). However, the extension to above atmospheric pressures is necessary for retaining stoichiometric single phase surface composition for materials that are characterized by large thermal decomposition pressures at optimum processing temperatures. For example,  $\text{Ga}_x\text{In}_{1-x}\text{N}$  heterostructures have been identified as an important basis for manufacturing of optoelectronic and microelectronic devices, such as, light sources, detectors and high power microwave devices for which large potential markets can be identified. Due to the high

**Keywords:** real-time monitoring, high-pressure CVD, gas phase kinetics, thin film epitaxy, new research

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thermal decomposition pressure of InN, these devices are at present limited to gallium-rich compositions. High nitrogen pressure has been demonstrated to suppress thermal decomposition of InN, but has not been applied yet in chemical vapor deposition or etching experiments. Because of the difficulty with maintaining stoichiometry at elevated temperature, current knowledge regarding thermodynamic data for InN, e.g., its melting point, temperature-dependent heat capacity, heat and entropy of formation are known with far less accuracy than for InP, InAs and InSb. Gaining access to these data will require the development of new real-time optical diagnostics, capable to obtain sufficient accurate data on flow conditions, gas phase reactions as well as on the surface reaction kinetic to support modeling and simulations of thin film growth under laminar and/or turbulent flow conditions at sub-atmospheric pressure.

The here-presented research focuses on the base material InN and addresses both: (a) the prediction and simulation of gas phase reactions and surface kinetics of InN growth at high pressures (up to 100 bar) and (b) real-time optical monitoring of gas phase- and surface chemistry processes during high pressure chemical vapor deposition (CVD) of InN. We describe the present status of our modeling and simulations efforts on gas phase and surface reactions kinetics for InN growth at high pressures, which is based on a numerical solution of nonlinear, coupled partial differential equations representing the conservation of momentum, energy and total mass as well as balances over the individual species involved in the InN deposition. The operating conditions modeled correspond to flow dominated by forced convection where  $Gr \ll Re^2$ . We also describe the capabilities of the implemented high-pressure CVD reactor and the real-time optical monitoring techniques available in this reactor.

### **High-pressure Reactor**

The growth of III-nitrides under HPCVD conditions with integrated optical diagnostics requires a complete new reactor design as well as new gas mixing and gas injection controls. Figure 1a) depicts a side view of the assembled HPCVD reactor with flow direction from right to left. The flow control panel depicted in Figure 1b) is fully computer interfaced and provides:

- the compression of the III- and V-gas sources ( $\leq 100\text{bar}$ ),
- the mixing of the gas sources and dilution of the gases in nitrogen carrier gas,
- the pulsed injection of all gas sources,
- the pressure control of the reactor in the pressure range of 1 to 100 bar.

The flow channel of HPCVD reactor has constant cross section from entrance to the exit with symmetric sapphire substrates arrangements in the upper and lower channel walls. Details in the design were reported previously[3]. Thus the bifurcation of nutrient fluxes to the top and bottom channel walls is symmetric to the center-line. Thus well behaved flow and deposition can be expected in the targeted pressure range. Pressure tests were performed up to 120 bar with flows from 10 slm to 50 slm. In the next step we interfaced the reactor to the gas injection panel shown in Figure 1b). The gas injection sequences are presently tested and optimize in timing and flows. An exact timing is not only important to avoid pressure fluctuations during the switching sequences, but also to synchronize the gas precursor injection with the optical monitoring techniques.

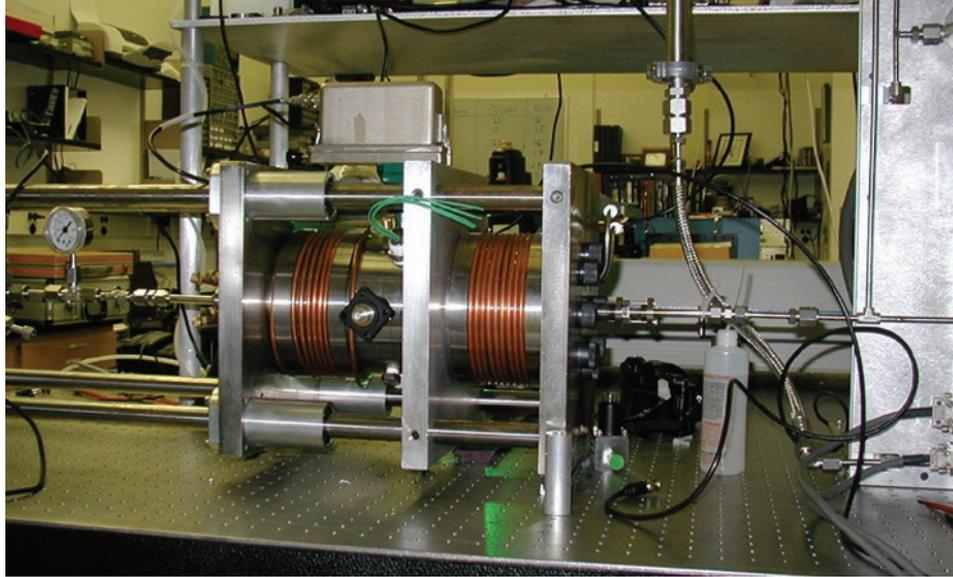


Figure 1a. Side view of the completely assembled HPCVD reactor with gas injection from the right. The optical monitoring plane is in the center of the substrates.

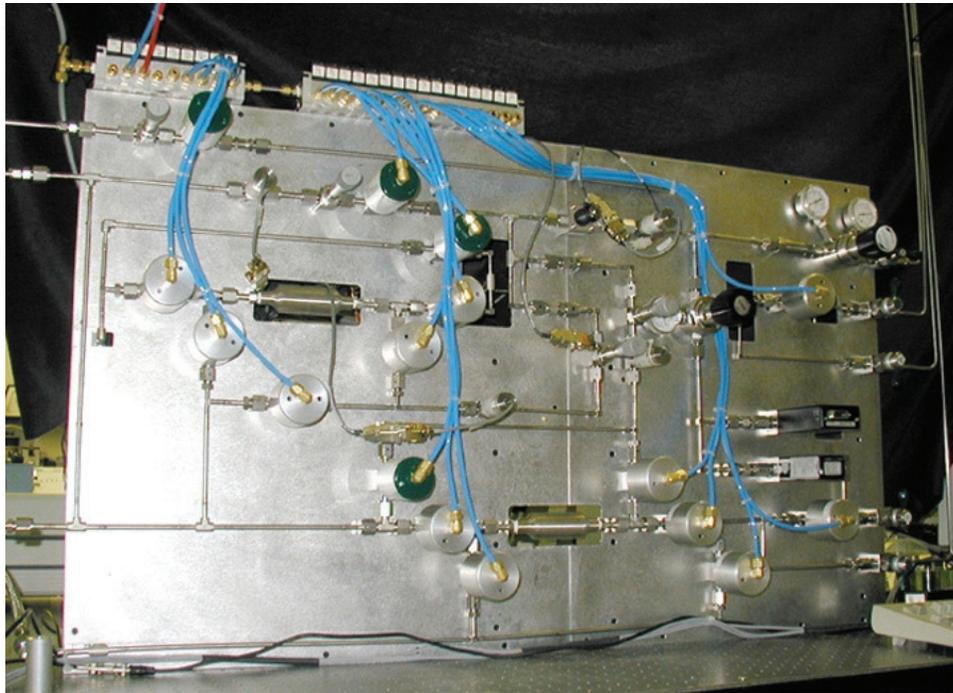


Figure 1b. Flow control panel for precursor compression and pulsed precursor gas injection.

For real-time gas flow dynamics studies as well as the analysis of the gas-phase decomposition kinetics during the thin film growth process, we integrated optical access ports in the reactor as schematically shown in Figure 2. The access ports allow the optical monitoring perpendicular to the flow direction at the center line of the two symmetric in the upper and lower channel walls inserted substrates. Two optical ports provide access to flow channel and allow the monitoring of gas flow and gas-phase decomposition kinetics. As depicted in Figure 3a, three ports in each half of the symmetric reactor provide access through the backside of the substrate to the growth surface and with it to the growth process itself. The optical rods

are made of sapphire and with its refractive index matched to the sapphire substrates. The rods are inserted through the outer reactor shell in the inner shell and touch the substrates from the back. The pressure is retained by a double o-ring seal within the outer reactor shell. A protective cap on the outer side of the holder prevents the rod from moving outwards.

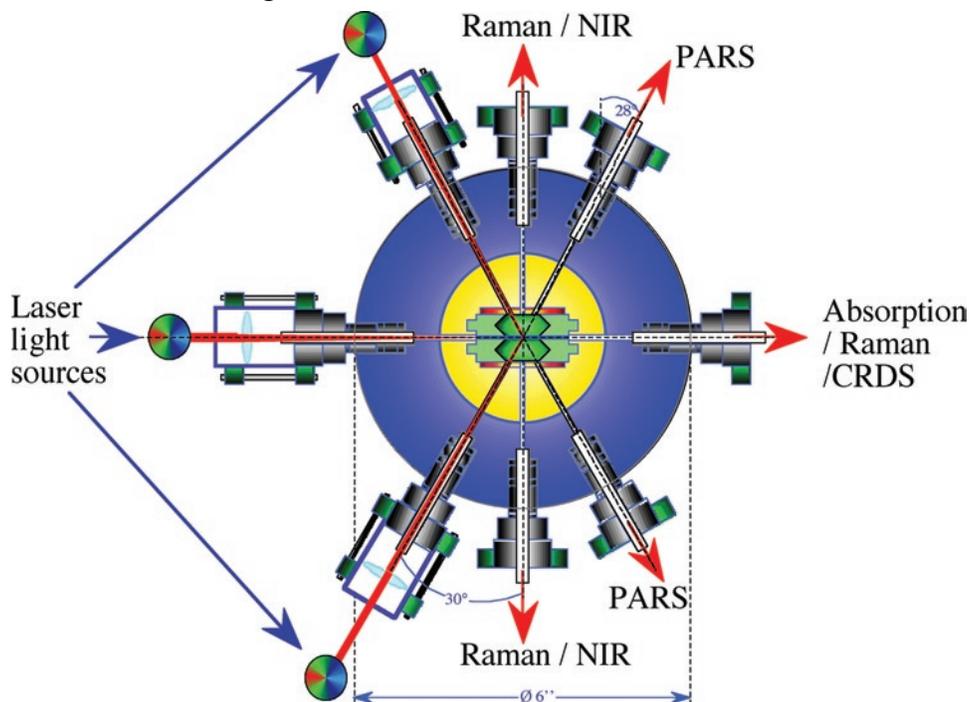


Figure 2. Cross Section of HPCVD reactor, which contains the integrated optical access ports. The cut is perpendicular to the flow channel.

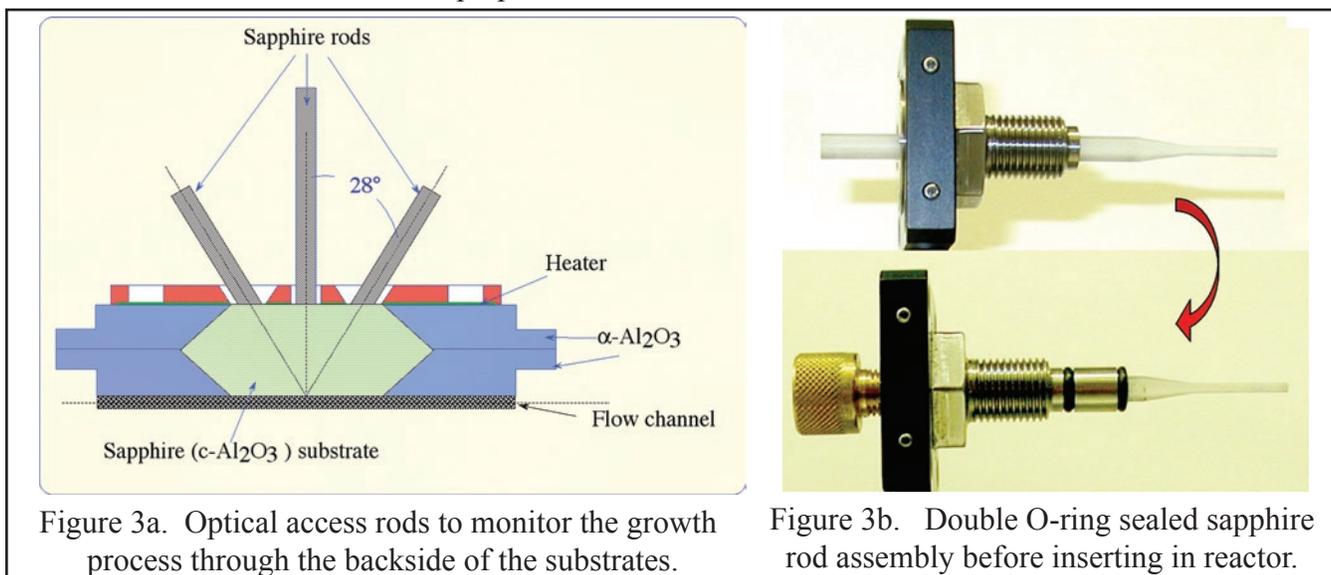


Figure 3a. Optical access rods to monitor the growth process through the backside of the substrates.

Figure 3b. Double O-ring sealed sapphire rod assembly before inserting in reactor.

The optical real-time monitoring capabilities will provide crucial experimental data as they are entering as input parameter for process models and simulation codes as well as to establish growth parameter sets needed for analysis and control of chemical vapor deposition at elevated pressure. Access to a microgravity environment will allow to retain laminar flow at high pressure conditions, which is essential

for successful acquisition and interpretation of the optical data. In the following, we present our modeling and simulations efforts on gas phase and surface reactions kinetics for InN growth at high pressures.

### Modeling and Simulations

The HPCVD reactor simulations are based on a numerical solution of nonlinear, coupled partial differential equations representing the conservation of momentum, energy and total mass as well as balances over the individual species. The modeling equations were solved using the finite volume element method based upon an integral form of the equations to be solved. The integration of the differential equations leads to a set of algebraic equations which are solved internally by the CFD-ACE(U) iterative, segregated solution method wherein the equation sets for each variable are solved sequentially and repeatedly until a converged solution is obtained. The operating conditions correspond to flow dominated by forced convection where  $Gr \ll Re^2$ . Details on the boundary conditions are given elsewhere[4]

The surface reaction mechanism for growth of InN has been described by a reduced-order model, noting that a larger number of possible reactions may have to be taken in account[5-7]. The reduced order model is based on pulsed chemical vapor deposition, which substantially reduces the number of reacting species. A typically precursor injection sequence is depicted in Figure 4. The V/III ratio has to be chosen properly to assure the incorporation of In-atoms supplied to the surface into the InN lattice. The assumed surface reactions are summarized in Table 1, showing the adsorption of the reactive species that are present in the gas phase, with rate parameters given by Cardelino et al.[8]. The growth of InN from trimethylindium (TMI) and ammonia ( $NH_3$ ) has been simulated based on the reduced-order model, with flow, heat and mass transfer in the HPCVD reactor evaluated for a symmetrical substrate wafers positioning.

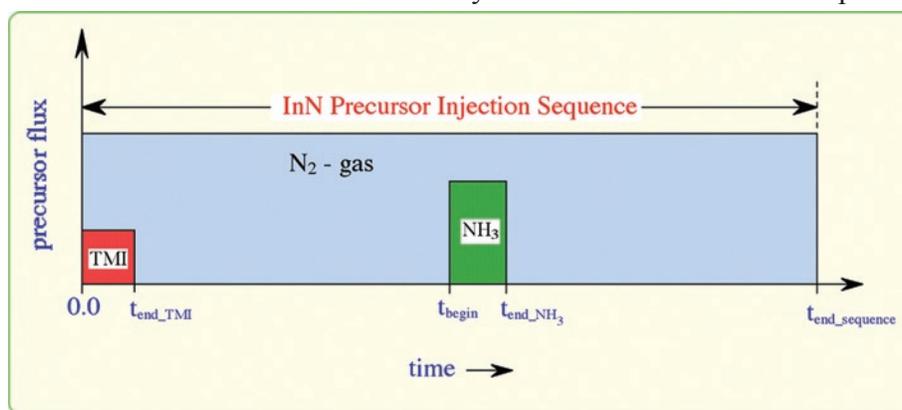


Figure 4. Schematic timing sequence for the precursor injection for InN growth.

The gas phase reactions of TMI according to Table 1 were obtained in the pressure range of 10 to 100 atm as a function of substrate temperature and centerline flow velocity under steady-state conditions. The predicted gas phase reaction variations with centerline flow velocity for  $p = 100$  atm and  $T_s = 900$  K are depicted in Figure 5. The simulations show the vapor phase concentration of MMI at the gas - substrate interface with  $p = 100$  atm,  $u = 12$  slm and  $T_s = 900$  K and with  $p = 10$  atm,  $u = 60$  slm and  $T_s = 900$  K, in Figures 5a and 5b, respectively. A comparison shows that for  $u = 12$  slm and  $p = 10$  atm the maximum concentration of MMI is at the center of the substrate (see Figure 5a), whereas for  $u = 60$  slm and  $p = 10$  atm, the maximum concentration of MMI has shifted downstream. The simulations indicate that for higher centerline velocities the maximum concentration of MMI will shift downstream, which would prevent the maximum MMI flux to become adsorbed at the center of the substrate. When the flow rates

increased to 120 slm at  $p = 10$  atm and  $T_s = 900$  K, the Re number equals 3000, which requires the use of the k-epsilon model to account for the effects of turbulence.

Table 1. Reduced-Order Model: Pulsed TMI followed by Pulsed  $\text{NH}_3$

<b>Gas Phase Reactions:</b>	$\text{TMI}(\text{g}) \rightarrow \text{DMI}(\text{g}) + \text{CH}_3$
	$\text{DMI}(\text{g}) \rightarrow \text{MMI}(\text{g}) + \text{CH}_3$
	$\text{NH}_3(\text{g}) + h\nu (170\text{-}220 \text{ nm}) \rightarrow \text{NH}(\text{g}) + \text{H}_2$
<b>Surface Reactions:</b>	$\text{MMI}(\text{g}) + \text{S}_1 \rightarrow \text{MMI}_{\text{ad}}$
	$\text{NH}(\text{g}) + \text{MMI}_{\text{ad}} \rightarrow (\text{HN:MMI})_{\text{ad}} \rightarrow \text{InN}(\text{s}) + \text{CH}_4 \uparrow$

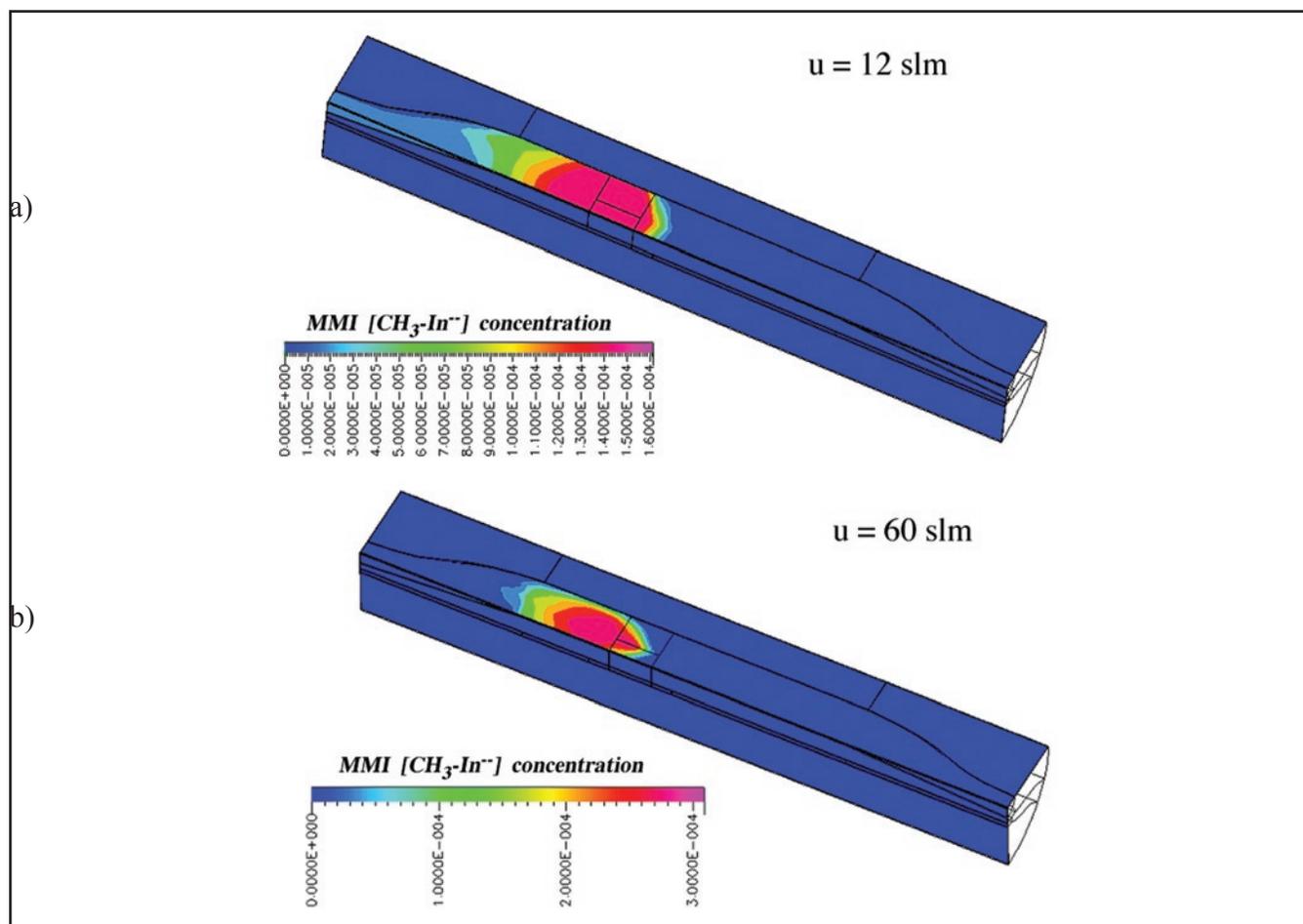


Figure 5. Effect of Centerline flow velocity for  $P = 100$  atm and  $T_s = 900$  K.

At the optimum growth temperature of  $T_s = 900$  K in the pressure range of 10 to 20 atm, the concentration of MMI and atomic indium is evenly distributed over the substrate surface as seen in Figures 6 (a-d), respectively. The effect of the increasing pressure on the gas phase kinetics is summarized in Figure 7 for a substrate temperature of 1000K and a centerline velocity  $u=12$  slm.

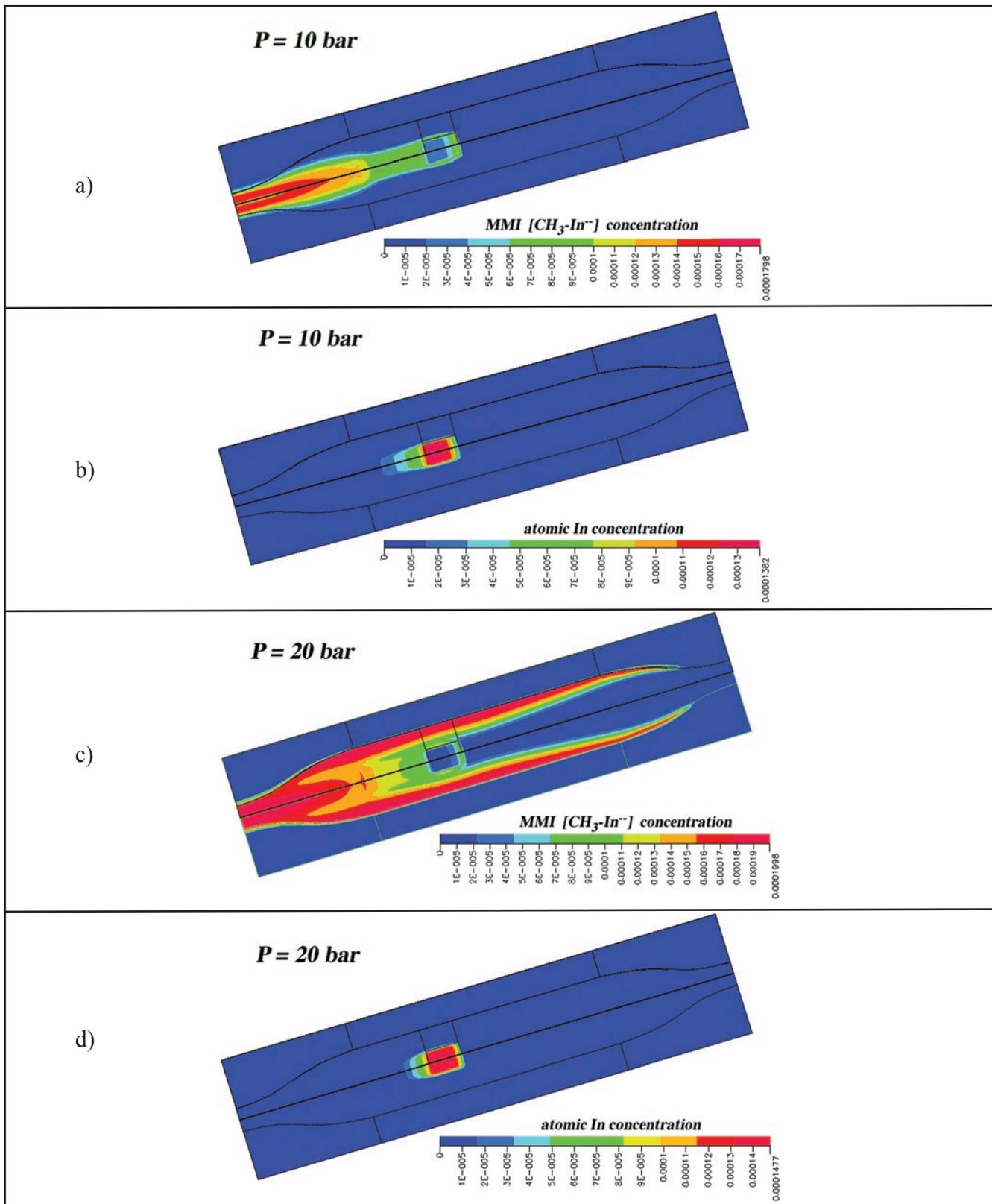


Figure 6. Trimethylindium (TMI) gas phase decomposition in monomethylindium (MMI) and atomic indium at 10 and 20 bar at a substrate temperature of 1000 K and a flow of 12 slm.

The most dominate changes in the DMI, MMI and atomic indium concentrations are expected in the pressure range between 1 and 20 atm. As depicted in Figure 7, a further pressure increase beyond 40 bar does not significantly alter the MMI and atomic indium concentration at the center of the substrate, which is accessible for experimental validation. These results are in good agreements with ab initio calculations by Cardelino et al.[9], which show in inversion of monomethylindium versus atomic indium concentration in the pressure range of 1 bar to 20 bars.

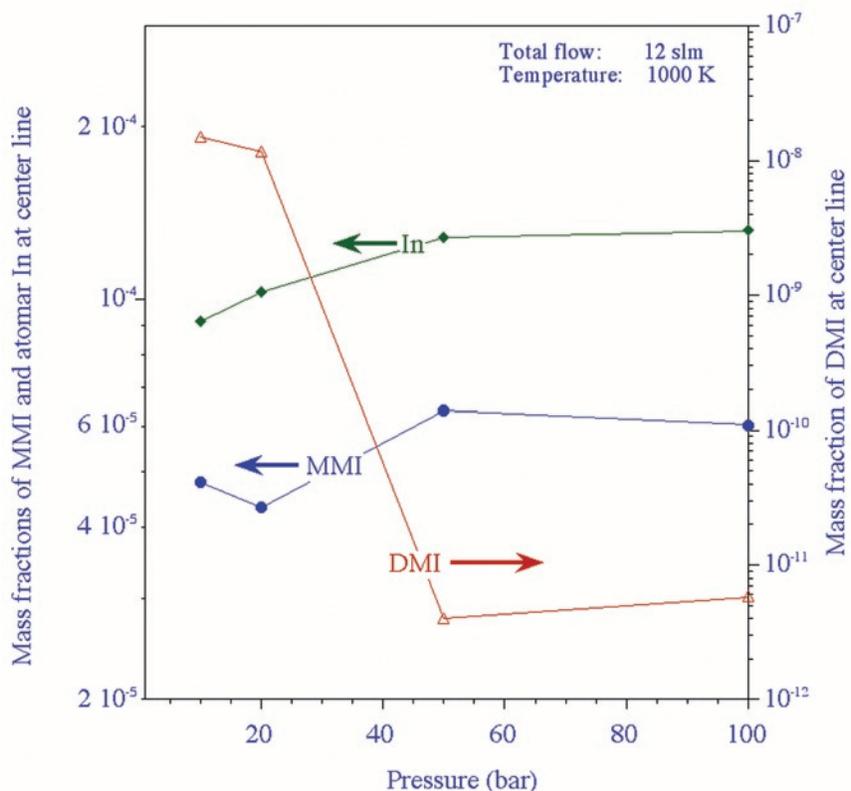


Figure 7. Effects of pressure on gas phase kinetics at  $T_s = 1000\text{K}$  and  $u = 12$  slm.

### InN Growth Rate Simulations

A 2-dim, time-dependent simulation model was used to combine the gas phase reactions and transport with surface reactions leading to InN formation using a pulsing sequence as illustrated in Figure 4. The timing of the precursor injection keeps the process gases separate and thus precludes homogeneous formation and transport of adducts in the gas phase. The injection sequence introduces  $N_2 + TMI$ ;  $N_2$ ;  $N_2 + NH_3$ ;  $N_2$ . into the reactor flow channel with an experimental limit of approximate 0.2 seconds.

Figure 8a illustrates the site fraction of MMI adsorbed to the surface as a function of time. As shown in Figure 7, the surface of the substrate is completely covered by MMI until NH is introduced and InN is formed. This film growth begins when NH is generated and interacts with the MMI covered substrate. The results are tentative in that experimental work needs to be done to validate the mechanisms selected and preliminary reaction rates theoretically derived.

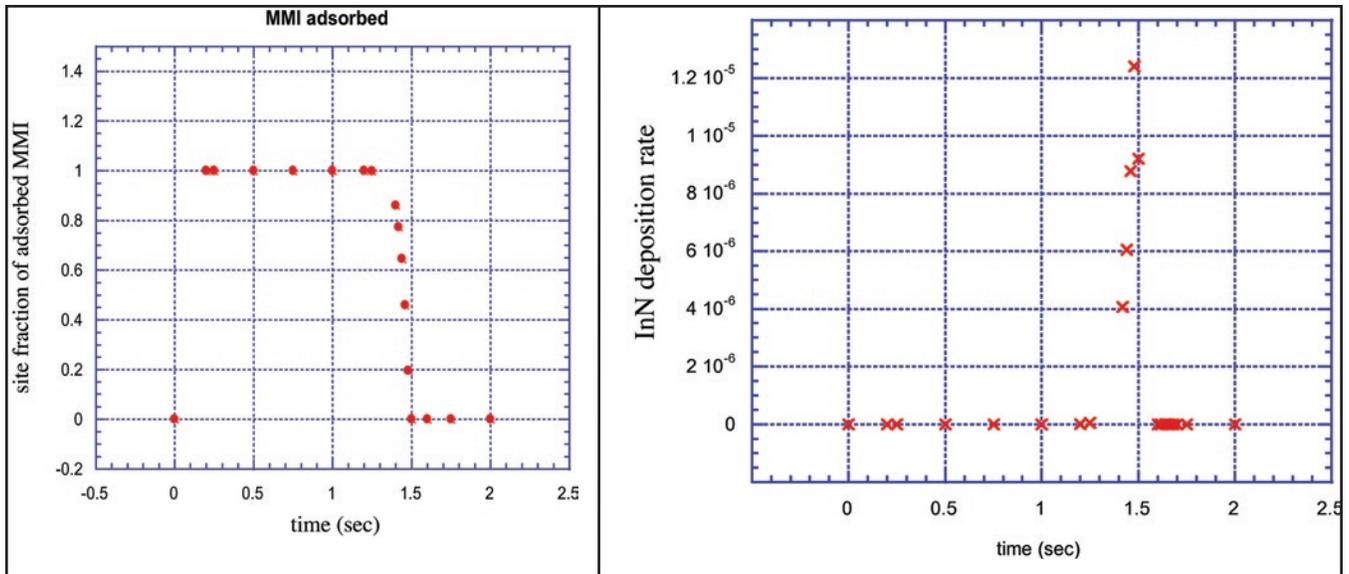


Figure 8. **a)** Site fraction of adsorbed MMI as a function of time. **b)** Deposition rate of InN vs. time at the center of the substrate.

### Acknowledgments

We would like to acknowledge support of this work by NASA cooperative Agreement NCC8-95 and NASA grant NAG8-1686.

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